

UTILITY PATENT APPLICATION TRANSMITTAL

Title of Invention

Novel Photoinitiators and Applications Therefor

Named Inventor(s)

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under 37 CFR 1.53(b))

APPLICATION ELEMENTS

1. ☐ Fee Transmittal Form
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Total Pages **67**
3. ☐ Drawings
Total Sheets _____
4. Oath or Declaration
Total Pages _____
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b. ☐ Copy from prior application (37 CFR 1.63(d))
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9. ☐ 37 CFR 3.73(b) Statement
(when there is an assignee)
☐ Power of Attorney by assignee
10. ☐ English Translation Document (if applicable)
11. ☐ Information Disclosure Statement (IDS)
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Status still proper and desired
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NOVEL PHOTOINITIATORS AND APPLICATIONS THEREFOR

Technical Field

The present invention relates to novel photoinitiators and methods for generating a reactive species using the photoinitiators. The present invention further relates to methods of polymerizing or photocuring polymerizable material using the above-mentioned photoinitiators. The photoinitiators of the present invention find particular utility in photocurable inks as used in ink jet printers or on a printing press with and without nitrogen blanketing.

Background of the Invention

Polymers have served essential needs in society. For many years, these needs were filled by natural polymers. More recently, synthetic polymers have played an increasingly greater role, particularly since the beginning of the 20th century. Especially useful polymers are those prepared by an addition polymerization mechanism, i.e., free radical chain polymerization of unsaturated monomers, and include, by way of example only, coatings and adhesives. In fact, the majority of commercially significant processes are based on free-radical chemistry. That is, chain polymerization is initiated by a reactive species, which often is a free radical. The source of the free radicals is termed an initiator or photoinitiator.

Improvements in free radical chain polymerization have focused both on (1) more reactive monomer and pre-polymer materials and (2) the photoinitiator. Whether a particular unsaturated monomer can be converted to a polymer requires structural, thermodynamic, and kinetic feasibility. Even when all three exist, kinetic feasibility is achieved in many cases only with a specific type of photoinitiator. Moreover, the photoinitiator can have a significant effect on reaction rate which, in turn, may determine the commercial success or failure of a particular polymerization process or product.

A free radical-generating photoinitiator may generate free radicals in several different ways. For example, the thermal, homolytic dissociation of an initiator typically directly yields two free radicals per initiator molecule. A photoinitiator, i.e., an initiator which absorbs light energy, may produce free radicals by one of three pathways:

(1) the photoinitiator undergoes excitation by energy absorption with subsequent decomposition into one or more radicals;

(2) the photoinitiator undergoes excitation and the excited species interacts with a second compound (by either energy transfer or a redox reaction) to form free radicals from the latter and/or former compound(s); or

(3) the photoinitiator undergoes an electron transfer to produce a radical cation and a radical anion.

While any free radical chain polymerization process should avoid the presence of species which may prematurely terminate the polymerization reaction, prior photoinitiators present special problems. For example, absorption of the light by the reaction medium may limit the amount of energy available for absorption by the photoinitiator. Also, the often competitive and complex kinetics involved may have an adverse effect on the reaction rate. Moreover, some commercially available radiation sources, such as medium

and high pressure mercury and xenon lamps, may emit over a wide wavelength range, thus producing individual emission bands of relatively low intensity. Many photoinitiators only absorb over a small portion of the emission spectra and, as a consequence, much of the lamps' radiation remains unused. In addition, most known photoinitiators have only moderate "quantum yields" (generally less than 0.4) at these wavelengths, indicating that the conversion of light radiation to radical formation can be more efficient.

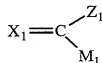
Many commercially available photoinitiators, including IRGACURE® 369, are presently used in ink compositions to accelerate ink drying in "radiation-drying printing." As used herein, the term "radiation-drying printing" refers to any printing method which utilizes radiation as a drying means. Radiation-drying printing includes, for example, off-set printing operations, such as on a Heidelberg press, flexographic printing, and flat-bed printing. Commercially available photoinitiator systems have a number of shortcomings. First, most of the commercially available photoinitiator systems require a relatively large amount of photoinitiator in the ink composition to fully cure/dry the ink composition. This leads to undesirable extractables within the ink composition. Second, most of the commercially available photoinitiator systems require a high energy radiation source to induce photocuring. Moreover, even with the high energy radiation source, often the cure results are unsatisfactory. Third, many commercially available photoinitiator systems are highly reactive to oxygen and must be used under a nitrogen blanket. Fourth, even with a large amount of photoinitiator and a high energy light source, the commercially available photoinitiator systems require a dry/cure time only accomplished by multiple passes, as many

as 15 passes, under a light source, which significantly limits the output of a radiation-drying printing press.

What is needed in the art is a new class of energy-efficient photoinitiators having unsurpassed photoreactivity even when exposed to a low energy light source, such as a 50 W excimer cold lamp. What is also needed in the art is a new class of energy-efficient photoinitiators that may be cured in air, as well as, a nitrogen atmosphere. Further, what is needed in the art is a class of photoinitiators having unsurpassed photoreactivity, for use in the radiation-drying printing industry, which will significantly increase the output of a radiation-drying printing press due to reduction in ink drying/curing time.

Summary of the Invention

The present invention addresses some of the difficulties and problems discussed above by the discovery of energy-efficient photoinitiators having the following general formula:



wherein X_1 is a conjugated system such as one or more aryl groups or substituted aryl groups; Z_1 is $-\text{O}$, $-\text{S}$, an alkyl group having from one to six carbon atoms, an ester moiety, a ketone moiety, an amine moiety, an imine moiety, an ether moiety, an aryl or substituted aryl group, a metal or non-metal, or a metal or non-metal containing group, such as a zinc-containing group or a boron-containing group, respectively; and M_1 is an alkyl group, a substituted alkyl group, or forms a five-member ring with Z_1 . By selecting particular " X_1 ", " Z_1 ", and " M_1 " groups, photoinitiators are produced having a desired absorption maximum, which

substantially corresponds to an emission band of a radiation source and selectively varies from less than about 222 nm to greater than about 445 nm.

5 The present invention is directed to the above-described photoinitiators, compositions containing the same, and methods for generating a reactive species which includes providing one or more of the photoinitiators and irradiating the one or more photoinitiators. One of the
10 main advantages of the photoinitiators of the present invention is that they efficiently generate one or more reactive species under extremely low energy lamps, such as excimer lamps and mercury lamps, as compared to prior art photoinitiators. The photoinitiators of the present
15 invention also efficiently generate one or more reactive species in air or in a nitrogen atmosphere. Unlike many prior photoinitiators, the photoinitiators of the present invention are not sensitive to oxygen. Further, the photoinitiators of the present invention are as much as ten
20 times faster than the best prior art photoinitiators.

20 The present invention is further directed to a method of efficiently generating a reactive species by matching a photoinitiator having an absorption maximum to an emission band of a radiation source, which corresponds to
25 the absorption maximum. By adjusting the substituents of the photoinitiator, one can shift the absorption maximum of the photoinitiator from less than about 222 nm to greater than 445 nm.

30 The present invention is also directed to methods of using the above-described photoinitiators to polymerize and/or photocure a polymerizable material. The photoinitiators of the present invention result in rapid curing times in comparison to the curing times of prior art
35 photoinitiators, even with relatively low output lamps. The present invention includes a method of polymerizing an polymerizable material by exposing the polymerizable

material to radiation in the presence of the efficacious wavelength specific photoinitiator composition described above. When an unsaturated oligomer/monomer mixture is employed, curing is accomplished.

5 The present invention further includes a film and a method for producing a film, by drawing an admixture of polymerizable material and one or more photoinitiators of the present invention, into a film and irradiating the film with an amount of radiation sufficient to polymerize the composition. The admixture may be drawn into a film on a nonwoven web or on a fiber, thereby providing a polymer-coated nonwoven web or fiber, and a method for producing the same.

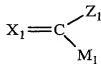
10 The present invention is also directed to an adhesive composition comprising a polymerizable material admixed with one or more photoinitiators of the present invention. Similarly, the present invention includes a laminated structure comprising at least two layers bonded together with the above-described adhesive composition, in which at least one layer is a nonwoven web or film. Accordingly, the present invention provides a method of laminating a structure wherein a structure having at least two layers with the above-described adhesive composition between the layers is irradiated to polymerize the adhesive composition.

15 The present invention is further directed to a method of printing, wherein the method comprises incorporating one or more photoinitiators of the present invention into an ink composition; printing the ink onto a substrate; and drying the ink with a source of radiation.

20 These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

Detailed Description of the Invention

The present invention is directed to energy-efficient, reactive, photoinitiators and methods for utilizing the same. More particularly, the present invention is directed to new photoinitiators having the following general formula:



wherein X_1 comprises a conjugated system such as one or more aryl groups or substituted aryl groups; Z_1 is $-\text{O}$, $-\text{S}$, an alkyl group having from one to six carbon atoms, an ester moiety, a ketone moiety, an amine moiety, an imine moiety, an ether moiety, an aryl or substituted aryl group, a metal or non-metal, or a metal or non-metal containing group, such as a zinc-containing group or a boron-containing group, respectively; and M_1 comprises an alkyl group, a substituted alkyl group, or forms a five-member ring with Z_1 .

The present invention is further directed to a method of efficiently generating a reactive species by matching a photoinitiator having an absorption maximum to an emission band of a radiation source, which corresponds to the absorption maximum. By adjusting the substituents of the photoinitiator, one can shift the absorption maximum of the photoinitiator from less than about 222 nm to greater than 445 nm.

The present invention also includes a method of polymerizing a polymerizable material by exposing the polymerizable material to electromagnetic radiation in the presence of one or more of the photoinitiators described above. Further, the present invention is directed to a film and a method for producing a film, by drawing an admixture of polymerizable material and one or more of the

photoinitiators described above, into a film and irradiating the film with an amount of electromagnetic radiation sufficient to polymerize the admixture.

5 The present invention is further directed to an adhesive composition comprising a polymerizable material admixed and one or more photoinitiators of the present invention. Similarly, the present invention includes a laminated structure comprising at least two layers bonded together with the above-described adhesive composition.
10 The present invention further provides a method of laminating a structure wherein a structure having at least two layers with the above-described adhesive composition between the layers is irradiated with appropriate electromagnetic radiation to polymerize the adhesive composition.
15

Definitions

As used herein, the term "reactive species" is used herein to mean any chemically reactive species including, but not limited to, free-radicals, cations, anions, nitrenes, and carbenes. Illustrated below are examples of several of such species. Examples of carbenes include, for example, methylene or carbene, dichlorocarbene, diphenylcarbene, alkylcarbonyl-carbenes, siloxycarbenes, and dicarbenes.
20 Examples of nitrenes include, also by way of example, nitrene, alkyl nitrenes, and aryl nitrenes. Cations (sometimes referred to as carbocations or carbonium ions) include, by way of illustration, a proton; primary, secondary, and tertiary alkyl carbocations, such as methyl cation, ethyl cation, propyl cation, *t*-butyl cation, *t*-pentyl cation, *t*-hexyl cation; allylic cations; benzylic cations; aryl cations, such as triphenyl cation; cyclopropylmethyl cations; methoxymethyl cation; triarylsulphonium cations; and acyl cations. Cations also include those formed from various
25 metal salts, such as tetra-*n*-butylammonium
30
35

tetrahaloaurate(III) salts; sodium tetrachloroaurate(III); vanadium tetrachloride; and silver, copper(I) and (II), and thallium(I) triflates. Examples of anions (sometimes referred to as carbanions) include, by way of example, alkyl anions, such as ethyl anion, *n*-propyl anion, isobutyl anion, and neopentyl anion; cycloalkyl anions, such as cyclopropyl anion, cyclobutyl anion, and cyclopentyl anion; allylic anions; benzylic anions; aryl cations; and sulfur- or phosphorus-containing alkyl anions. Finally, examples of organometallic photoinitiators include titanocenes, fluorinated diaryltitanocenes, iron arene complexes, manganese decacarbonyl, and methylcyclopentadienyl manganese tricarbonyl. Organometallic photoinitiators generally produce free radicals or cations.

As used herein, the term "quantum yield" is used herein to indicate the efficiency of a photochemical process. More particularly quantum yield is a measure of the probability that a particular molecule will absorb a quantum of light during its interaction with a photon. The term expresses the number of photochemical events per photon absorbed. Thus, quantum yields may vary from zero (no absorption) to 1.

As used herein, the term "polymerization" is used herein to mean the combining, e.g. covalent bonding, of a number of smaller molecules, such as monomers, to form large molecules, i.e., macromolecules or polymers. The monomers may be combined to form only linear macromolecules or they may be combined to form three-dimensional macromolecules, commonly referred to as crosslinked polymers.

As used herein, the term "curing" means the polymerization of functional oligomers and monomers, or even polymers, into a crosslinked polymer network. Thus, curing is the polymerization of unsaturated monomers or oligomers in the presence of crosslinking agents.

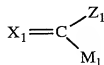
As used herein, the terms "unsaturated monomer," "functional oligomer," and "crosslinking agent" are used herein with their usual meanings and are well understood by those having ordinary skill in the art. The singular form of each is intended to include both the singular and the plural, i.e., one or more of each respective material.

As used herein, the term "unsaturated polymerizable material" is meant to include any unsaturated material capable of undergoing polymerization. The term encompasses unsaturated monomers, oligomers, and crosslinking agents. Again, the singular form of the term is intended to include both the singular and the plural.

As used herein, the term "fiber" as used herein denotes a threadlike structure. The fibers used in the present invention may be any fibers known in the art. As used herein, the term "nonwoven web" as used herein denotes a web-like matter comprised of one or more overlapping or interconnected fibers in a nonwoven manner. It is to be understood that any nonwoven fibers known in the art may be used in the present invention.

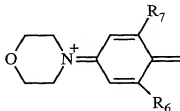
Photoinitiators

The present invention is directed to new photoinitiators having the following general formula:

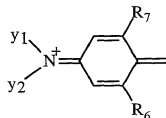


wherein X_1 is a conjugated system such as one or more aryl groups or substituted aryl groups; Z_1 is $-\text{O}-$, $-\text{S}-$, an alkyl group having from one to six carbon atoms, an ester moiety, a ketone moiety, an amine moiety, an imine moiety, an ether moiety, an aryl or substituted aryl group, a metal or non-metal, or a metal or non-metal containing group, such as a

zinc-containing group or a boron-containing group, respectively; and M_1 is an alkyl group, a substituted alkyl group, or forms a five-member ring with Z_1 . In one embodiment of the present invention, X_1 comprises



or



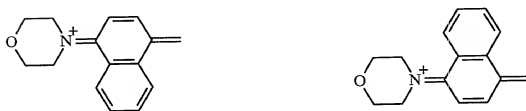
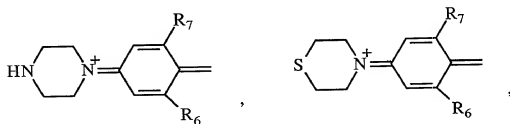
wherein R_6 and R_7 each independently represent hydrogen, an alkyl group having from one to six carbon atoms, an alkoxy group having from one to six carbon atoms, or a halogen-substituted alkyl group; and wherein y_1 and y_2 each independently represent a hydrogen, an alkyl group having from one to six carbon atoms, an aryl group,



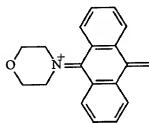
or



wherein X_3 represents a hydrogen, an alkyl or substituted alkyl group, or an aryl or substituted aryl group. Other suitable X_1 groups include, but are not limited to, the following:



or



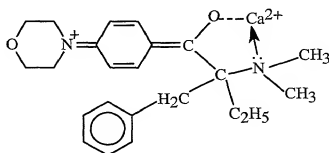
Desirably, R_6 and R_7 each independently represent a methyl group, an ethyl group, an isopropyl group, a methoxy group, an ethoxy group, or a trifluoromethyl group.

In a further embodiment of the present invention, M_1 comprises a tertiary alkyl group having the following formula:



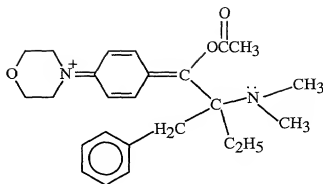
wherein y_3 , y_4 and y_5 each independently represent a hydrogen, an alkyl group having from one to six carbon atoms, a tertiary amine group, an aryl group, or a substituted aryl group.

In one embodiment of the present invention, the photoinitiator has the following structure:

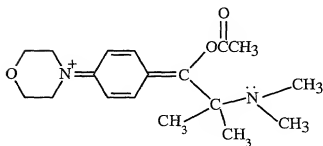


In the above structure, a calcium ion forms a five member ring, which includes the oxygen atom (" Z_1 ") and the electron-rich nitrogen atom. As used herein, an arrow represents a coordinate covalent bond between an electron-rich nitrogen atom and a metal or non-metal cation. It should be understood that other cations may be used instead of the calcium ion. Other suitable cations include, but are not limited to, beryllium, magnesium, strontium, barium, zinc, aluminum, and copper (II).

In a further embodiment, Z_1 in the above-described general formula comprises an ester moiety. Examples of such photoinitiators include, but are not limited to, photoinitiators having the following structure:

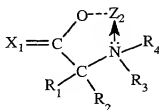


or



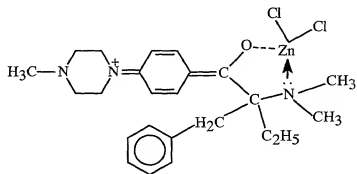
In the above photoinitiators, it should be noted that the $-\text{C}(\text{O})\text{CH}_3$ group ("Z₁") may be substituted with other groups including, but not limited to, $-\text{CH}_3$, $-\text{BF}_3$ and phenyl groups.

In yet a further embodiment, the photoinitiators of the present invention have the following general formula:

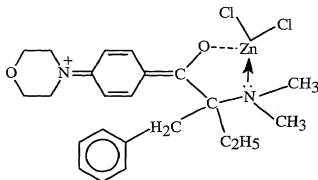


wherein X_1 is as defined above; Z_2 is a metal or non-metal cation, such as Zn^{2+} , Ca^{2+} , or boron, or a salt thereof, or $-C(O)R$, which forms a covalent bond with the oxygen

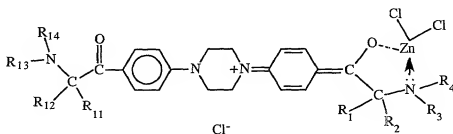
5 Photoinitiators having the above formula include, but are not limited to, the following photoinitiators:



and

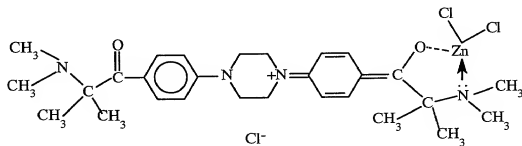


10 One photoinitiator of particular interest, having the above
general formula, is shown below:

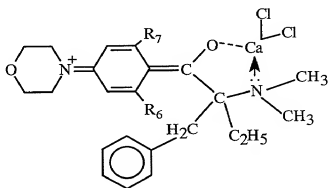


wherein R_{11} , R_{12} , R_{13} , and R_{14} are each independently a hydrogen atom; an alkyl group or substituted alkyl group.

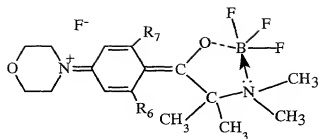
In one embodiment of the present invention, the photoinitiator has the following structure:



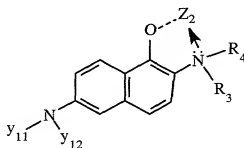
In a further embodiment of the present invention, the photoinitiator has the following structure:



In the above structure, the calcium atom forms a five member ring, which includes the oxygen atom and the electron-rich nitrogen atom. It should be understood that other salts may be used instead of the calcium chloride. Other suitable salts include, but are not limited to, salts containing beryllium, magnesium, strontium, barium, zinc, aluminum, scandium, and copper (II). For example, another photoinitiator of the present invention may have the following structure:



In a further embodiment of the present invention, R_1 , R_2 , and X_1 of the above-described general formula form one or more aromatic rings to form a photoinitiator having the structure below:



wherein Z_2 , R_3 , and R_4 are substituents as defined above and y_{11} and y_{12} are each independently represent a hydrogen; an alkyl group having from one to six carbon atoms; an aryl group;



or



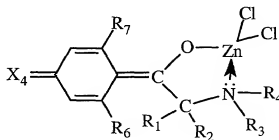
5 wherein X_3 is defined above.

The present invention is further directed to novel photoinitiators having the following general formula:

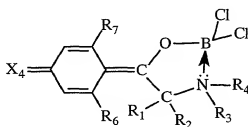


10 wherein Y is $-\text{O}-$ or $-\text{N}(\text{R}_5)-$; Z_3 is a metal or nonmetal cation or a salt containing the cation; and X_1 , R_1 , R_2 , R_3 , R_4 , and R_5 are as defined above. Suitable Z_3 groups include, but are not limited to, metals and metal salts containing Cd, Hg, Zn, Al, Ga, In, Tl, Sc, Ge, Pb, Si, Ti, Sn, and Zr, as well as, nonmetals and nonmetal salts containing boron and phosphorus. Desirably, Z_3 comprises a chloride-containing salt such as zinc chloride, zinc benzyl chloride, or boron chloride. Desirably, "R" comprises hydrogen, a methyl group, an ethyl group, a propyl group, or a benzyl group.

20 In one embodiment of the present invention, the photoinitiator has the following structure:

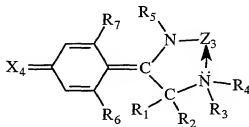


wherein X_4 comprises any nitrogen-containing group, which donates a pair of electrons to the nitrogen-carbon double bond; and R_1 , R_2 , R_3 , R_4 , R_6 , and R_7 are as defined above. The above photoinitiator has an absorption maximum of about 360 nm. In a further embodiment of the present invention, the photoinitiator has the following structure:

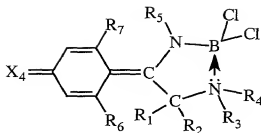


wherein X_4 , R_1 , R_2 , R_3 , R_4 , R_6 , and R_7 are as defined above. By replacing the zinc chloride with boron chloride, the absorption maximum of the photoinitiator shifts to about 410 nm.

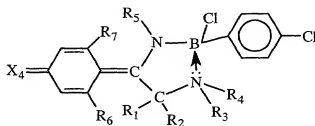
Other photoinitiators of the present invention have the following structure:



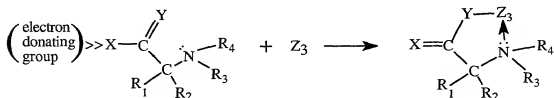
wherein X_4 , R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are as defined above. In one embodiment of the present invention, the photoinitiator has the following structure:



wherein X_4 , R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are as defined above. By replacing the oxygen atom with a nitrogen atom in the five member ring, the absorption maximum of the photoinitiator shifts further to greater than about 410 nm. It should be noted that other metal and nonmetal salts may be used in place of the metal and nonmetal chlorides. For example, the above photoinitiator may have the following structure:



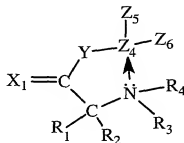
The above-described photoinitiators of the present invention may be produced by the following reaction mechanism:



wherein a first compound reacts with a metal or metal salt or a nonmetal or nonmetal salt, Z_3 , to produce a

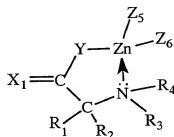
photoinitiator of the present invention, having a five-member ring containing a metal or nonmetal atom, at least one nitrogen atom, two carbon atoms, and possibly an oxygen atom.

- 5 In a further embodiment of the present invention, the photoinitiators have the following general formula:

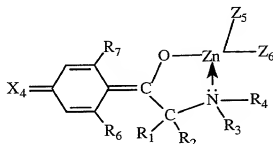


- 10 wherein X_1 , Y, R_1 , R_2 , R_3 , R_4 , and R_5 are as defined above; Z_4 is a metal or nonmetal atom; and Z_5 and Z_6 are halogen-containing anions or form one or more rings with or without R_3 or R_4 . In the above photoinitiator structure, the nitrogen atom donates its lone electron pair to metal or nonmetal atom, Z_4 , to form a five member ring. Suitable, Z_4 groups include, but are not limited to, metals such as Cd, Hg, Zn, Mg, Al, Ga, In, Tl, Sc, Ge, Pb, Si, Ti, Sn and Zr, as well as, nonmetals such as boron and phosphorus. Desirably, Z_4 comprises Cd, Zn, Mg, Ti, boron or phosphorus. More desirably, Z_4 comprises Zn. Suitable Z_5 and Z_6 groups include, but are not limited to, halogen-containing anions. Desirably, Z_5 and Z_6 each independently comprise fluorine, chlorine or bromine-containing anions. More desirably, Z_5 and Z_6 each independently comprise fluorine-containing anions. Even more desirably, Z_5 and Z_6 each independently comprise BF_4^- , AsF_6^- , PF_6^- , or SbF_6^- . Desirably, R_1 , R_2 , R_3 , and R_4 each independently comprise hydrogen, a methyl group, an ethyl group, a propyl group, or a benzyl group.
- 15
- 20
- 25

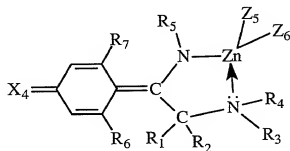
In one embodiment of the present invention, the photoinitiator has the following structure:



- 5 wherein X_1 , Y , R_1 , R_2 , R_3 , R_4 , Z_5 , and Z_6 are as defined above. In a further embodiment of the present invention, the photoinitiator has the following structure:

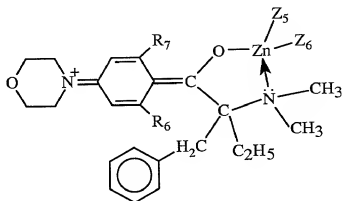


- 10 wherein X_4 , R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , Z_5 , and Z_6 are as defined above. Other photoinitiators of the present invention have the following structure:

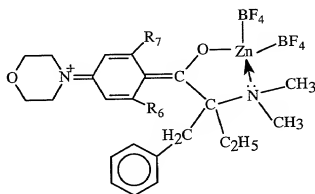


wherein X_4 , R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , Z_5 , and Z_6 are as defined above.

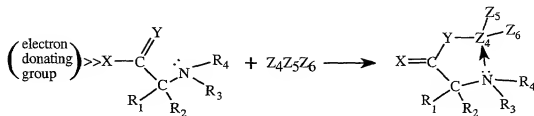
In yet a further embodiment, the photoinitiator of the present invention has the following structure:



wherein Z_5 and Z_6 are as defined above. In a further embodiment of the present invention, the photoinitiator of the present invention has the following structure:

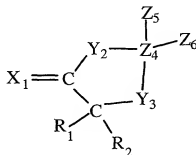


The above-described photoinitiators of the present invention may be produced by the following reaction mechanism:

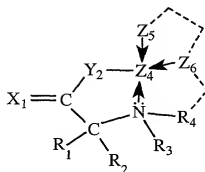


wherein a first compound reacts with a metal or nonmetal salt, $\text{Z}_4\text{Z}_5\text{Z}_6$, to produce a photoinitiator of the present invention, having a five-member ring containing a metal or nonmetal atom, at least one nitrogen atom, two carbon atoms, and possibly an oxygen atom.

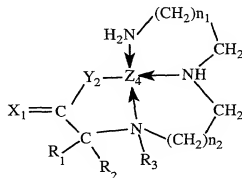
The present invention is further directed to novel photoinitiators having the following general structure:



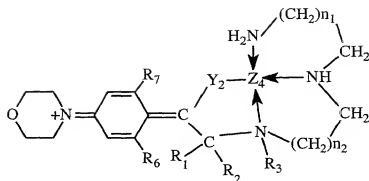
wherein Y_2 and Y_3 each independently represent $-\text{O}-$ or $-\text{N}(\text{R}_3)(\text{R}_4)-$; and X_1 , R_1 , R_2 , R_3 , R_4 , Z_4 , Z_5 , and Z_6 are as defined above. In one embodiment of the present invention, Y_3 represents $-\text{N}(\text{R}_3)(\text{R}_4)-$ and Z_5 and Z_6 form two five member rings: one five member ring which includes Z_4 , Z_5 , and Z_6 , and one five member rings which includes with Z_4 , Z_6 and one of R_3 or R_4 . The resulting photoinitiator has the following structure:



wherein Z_5 , Z_6 and R_4 comprise any combination of carbon, nitrogen and oxygen atoms to form two five member rings. It should be noted that Z_5 , Z_6 and R_4 may form two similar ring structures or two different ring structures. Also, each ring formed by Z_5 , Z_6 and R_4 may contain more than five ring members. In one embodiment of the present invention, the resulting photoinitiator has the following structure:

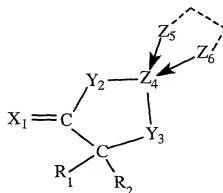


wherein X_1 , Y_2 , R_1 , R_2 , R_3 , and Z_4 are as defined above; and n_1 and n_2 each independently represent an integer from 1 to 5. Desirably, the resulting photoinitiator has the following structure:



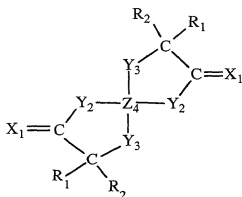
wherein R_1 , R_2 , R_3 , R_6 , R_7 , n_1 , and n_2 are as defined above.

- 5 In a further embodiment of the present invention, Z_5 and Z_6 form a single ring. The resulting photoinitiator has the following structure:



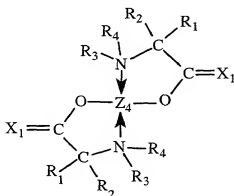
- 10 wherein Z_5 and Z_6 comprise any combination of carbon, nitrogen and oxygen atoms to form a ring. In one embodiment of the present invention, Z_5 and Z_6 form a five member ring so that the resulting photoinitiator has a dimeric structure. One example of the resulting photoinitiator has the following structure:

15



5 wherein X_1 , Y_2 , Y_3 , Z_4 , R_1 and R_2 are as defined above.

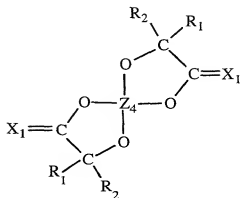
Other photoinitiators of the present invention having the above-described structure include, but are not limited to, the following photoinitiators:



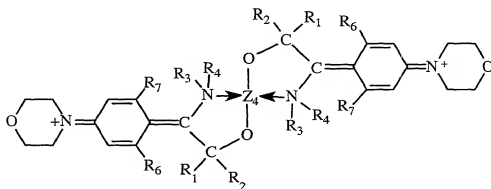
10

and

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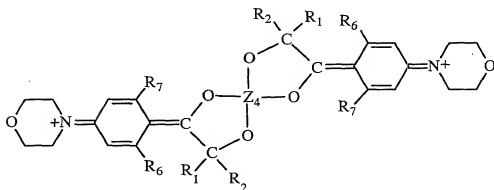


wherein X_1 , Z_4 , R_1 and R_2 are as defined above. Other desirable photoinitiators include, but are not limited to, the following photoinitiators:



5

and



wherein Z_4 , R_1 , R_2 , R_3 , R_4 , R_6 and R_7 are as defined above. Desirably, Z_4 comprises boron or zinc in the dimeric

structures above. It should be understood that the above dimeric structures are only examples of suitable dimeric structures for the photoinitiators of the present invention. Any combination of "X₁", "Z", "Y", and "R" groups may be used to form suitable dimeric structures for the photoinitiators of the present invention.

The resulting photoinitiators are relatively stable at room temperature (from about 15°C to 25°C) and normal room humidity (from about 5% to 60%; desirably from 5% to 30%). However, upon exposure to radiation at an appropriate wavelength, the photoinitiators efficiently produce one or more reactive species. The photoinitiators of the present invention have a high intensity of absorption. For example, the photoinitiators of the present invention have a molar extinction coefficient (absorptivity) greater than about 20,000 l mole⁻¹cm⁻¹. As a further example, the photoinitiators of the present invention have a molar extinction coefficient greater than about 25,000 l mole⁻¹cm⁻¹.

Method of Generating a Reactive Species and Applications Therefor

The present invention is further directed to a method of generating a reactive species. The method of generating a reactive species involves generating a reactive species by exposing one or more of the above-described photoinitiators to radiation. The exposure of the photoinitiators to a radiation source triggers a photochemical process. As stated above, the term "quantum yield" is used herein to indicate the efficiency of a photochemical process. More particularly, quantum yield is a measure of the probability that a particular molecule (photoinitiator) will absorb a quantum of light during its interaction with a photon. The term expresses the number of photochemical events per photon absorbed. Thus, quantum yields may vary from zero (no absorption) to 1.

The photoinitiators of the present invention absorb photons having a relatively specific wavelength and transfers the absorbed energy to one or more excitable portions of the molecule. The excitable portion of the molecule absorbs enough energy to cause a bond breakage, which generates one or more reactive species. The efficiency with which a reactive species is generated with the photoinitiators of the present invention is significantly greater than that experienced with photoinitiators of the prior art as indicated by faster cure times. For example, the photoinitiators of the present invention desirably will have a quantum yield greater than about 0.8. More desirably, the quantum yield of the photoinitiators of the present invention will be greater than about 0.9. Even more desirably, the quantum yield of the photoinitiators of the present invention will be greater than about 0.95. Still more desirably, the quantum yield of the photoinitiators of the present invention will be greater than about 0.99, with the most desirable quantum yield being about 1.0.

Exposing the photoinitiators of the present invention to radiation results in the generation of one or more reactive species. Thus, the photoinitiators may be employed in any situation where reactive species are required, such as for the polymerization of an unsaturated monomer and the curing of an unsaturated oligomer/monomer mixture. The unsaturated monomers and oligomers may be any of those known to one having ordinary skill in the art. In addition, the polymerization and curing media also may contain other materials as desired, such as pigments, extenders, amine synergists, and such other additives as are well known to those having ordinary skill in the art.

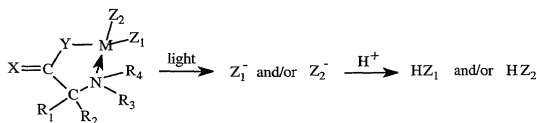
By way of illustration only, examples of unsaturated monomers and oligomers include ethylene, propylene, vinyl chloride, isobutylene, styrene, isoprene, acrylonitrile, acrylic acid, methacrylic acid, ethyl acrylate, methyl

methacrylate, vinyl acrylate, allyl methacrylate, tripropylene glycol diacrylate, trimethylol propane ethoxylate acrylate, epoxy acrylates, such as the reaction product of a bisphenol A epoxide with acrylic acid; polyether acrylates, such as the reaction product of acrylic acid with an adipic acid/ hexanediol-based polyether, urethane acrylates, such as the reaction product of hydroxypropyl acrylate with diphenylmethane-4,4'-diisocyanate, and polybutadiene diacrylate oligomer.

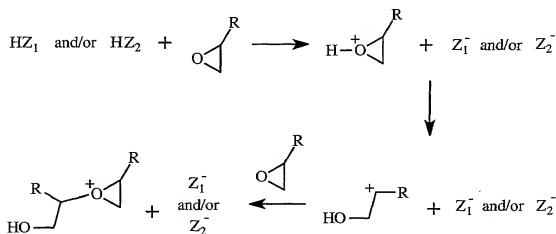
The types of reactions that various reactive species enter into include, but are not limited to, addition reactions, including polymerization reactions; abstraction reactions; rearrangement reactions; elimination reactions, including decarboxylation reactions; oxidation-reduction (redox) reactions; substitution reactions; and conjugation/deconjugation reactions.

Accordingly, the present invention also comprehends a method of polymerizing a polymerizable material, such as an unsaturated monomer or epoxy compound, by exposing the polymerizable material to radiation in the presence of the efficacious photoinitiators of the present invention described above. When an unsaturated oligomer/monomer mixture is employed in place of an unsaturated monomer, curing is accomplished. It is to be understood that the polymerizable material admixed with the photoinitiators of the present invention is to be admixed by means known in the art, and that the mixture will be irradiated with an amount of radiation sufficient to polymerize the material. The amount of radiation sufficient to polymerize the material is readily determinable by one of ordinary skill in the art, and depends upon the identity and amount of photoinitiators, the identity and amount of the polymerizable material, the intensity and wavelength of the radiation, and the duration of exposure to the radiation.

- 5 In one embodiment of the present invention, one or more photoinitiators of the present invention are used to polymerize an epoxy resin. It is believed that the following reaction mechanism takes place in the presence of a hydrogen-donating compound, such as an alcohol, cumene or amine:



- 10 Reactive species, HZ_1 and/or HZ_2 , then react with an epoxy resin according to the following mechanism to produce a polyether:





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photoinitiator, the identity and amount of the polymerizable material, the thickness of the admixture, the intensity and wavelength of the radiation, and duration of exposure to the radiation.

5 The present invention also includes an adhesive composition comprising a polymerizable material admixed with one or more photoinitiators of the present invention. Similarly, the present invention includes a laminated structure comprising at least two layers bonded together
10 with the above-described adhesive composition. In one embodiment of the present invention, a laminate is produced wherein at least one layer is a cellulosic or polyolefin nonwoven web or film. Accordingly, the present invention provides a method of laminating a structure
15 wherein a structure having at least two layers with the above-described adhesive composition between the layers is irradiated to polymerize the adhesive composition. When the unsaturated polymerizable material in the adhesive is an unsaturated oligomer/monomer mixture, the adhesive is
20 irradiated to cure the composition.

It is to be understood that any layers may be used in the laminates of the present invention, on the condition that at least one of the layers allows sufficient radiation to penetrate through the layer to enable the admixture to
25 polymerize sufficiently. Accordingly, any cellulosic or polyolefin nonwoven web or film known in the art may be used as one of the layers so long as they allow radiation to pass through. Again, the amount of radiation sufficient to polymerize the admixture is readily determinable by one of
30 ordinary skill in the art, and depends upon the identity and amount of photoinitiator, the identity and amount of the polymerizable material, the thickness of the admixture, the identity and thickness of the layer, the intensity and wavelength of the radiation, and the duration of exposure
35 to the radiation.

The radiation to which the photoinitiators of the present invention may be exposed generally will have a wavelength of from about 4 to about 1,000 nanometers. Thus, the radiation may be ultraviolet radiation, including near ultraviolet and far or vacuum ultraviolet radiation; visible radiation; and near infrared radiation. Desirably, the radiation will have a wavelength of from about 100 to about 900 nanometers. More desirably, the radiation will have a wavelength of from about 100 to 700 nanometers. Desirably, the radiation will be ultraviolet radiation having a wavelength of from about 4 to about 400 nanometers. More desirably, the radiation will have a wavelength of from about 100 to about 420 nanometers, and even more desirably will have a wavelength of from 320 to about 420 nanometers. The radiation desirably will be incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp or radiation from a mercury lamp.

Excimers are unstable excited-state molecular complexes which occur only under extreme conditions, such as those temporarily existing in special types of gas discharge. Typical examples are the molecular bonds between two rare gaseous atoms or between a rare gas atom and a halogen atom. Excimer complexes dissociate within less than a microsecond and, while they are dissociating, release their binding energy in the form of ultraviolet radiation. The dielectric barrier excimers in general emit in the range of from about 125 nm to about 500 nm, depending upon the excimer gas mixture.

Dielectric barrier discharge excimer lamps (also referred to hereinafter as "excimer lamp") are described, for example, by U. Kogelschatz, "Silent discharges for the generation of ultraviolet and vacuum ultraviolet excimer radiation." Pure & Appl. Chem., 62, No. 9, pp. 1667/1674 (1990); and E. Eliasson and U. Kogelschatz, "UV Excimer Radiation from Dielectric- Barrier Discharges." Appl. Phys.

B. 46, pp. 299-303 (1988). Excimer lamps were developed by ABB Infocom Ltd., Lenzburg, Switzerland, and at the present time are available from Heraeus Noblelight GmbH, Kleinostheim, Germany.

5 The excimer lamp emits incoherent, pulsed ultraviolet radiation. Such radiation has a relatively narrow bandwidth, i.e., the half width is of the order of approximately 5 to 100 nanometers. Desirably, the radiation will have a half width of the order of
10 approximately 5 to 50 nanometers, and more desirably will have a half width of the order of 5 to 25 nanometers. Most desirably, the half width will be of the order of approximately 5 to 15 nanometers.

15 The ultraviolet radiation emitted from an excimer lamp can be emitted in a plurality of wavelengths, wherein one or more of the wavelengths within the band are emitted at a maximum intensity. Accordingly, a plot of the wavelengths in the band against the intensity for each wavelength in the band produces a bell curve. The "half
20 width" of the range of ultraviolet radiation emitted by an excimer lamp is defined as the width of the bell curve at 50% of the maximum height of the bell curve.

25 The emitted radiation of an excimer lamp is incoherent and pulsed, the frequency of the pulses being dependent upon the frequency of the alternating current power supply which typically is in the range of from about 20 to about 300 kHz. An excimer lamp typically is identified or referred to by the wavelength at which the maximum
30 intensity of the radiation occurs, which convention is followed throughout this specification and the claims. Thus, in comparison with most other commercially useful sources of ultraviolet radiation which typically emit over the entire ultraviolet spectrum and even into the visible region, excimer lamp radiation is essentially monochromatic.

Although excimer lamps are highly desirable for use in the present invention, the source of radiation used with the photoinitiators of the present invention may be any radiation source known to those of ordinary skill in the art.

5 In a further embodiment of the present invention, a mercury lamp with a D-bulb, which produces radiation having an emission peak of about 360 nm is used to produce free radicals from the above-described photoinitiators. This radiation source is particularly useful when matched with

10 one or more photoinitiators of the present invention having an absorption maximum of about 360 nanometers, corresponding to the emission peak of the mercury lamp. Other specialty doped lamps, which emit radiation at about 420 nm, may be used with photoinitiators of the present invention which have an absorption maximum at about 420 nm. One lamp, the V-bulb available from Fusion Systems, is another suitable lamp for use in the present invention. In addition, specialty lamps having a specific emission band may be manufactured for use with one or more specific

15 photoinitiators of the present invention. New lamp technology provides the following potential advantages:

- (a) substantially single wavelength output;
- (b) unique wavelength output;
- (c) high intensity; and
- (d) absence of radiation trapping.

As a result of the photoinitiators of the present invention absorbing radiation in the range of about 250 to about 390 nanometers, some of the photoinitiators of the present invention will generate one or more reactive species upon exposure to sunlight. Accordingly, these photoinitiators of the present invention provides a method for the generation of reactive species that does not require the presence of a special light source.

The photoinitiators of the present invention enable the production of adhesive and coating compositions that consumers can apply to a desired object and polymerize or cure upon exposure to sunlight. These photoinitiators also enable numerous industry applications wherein polymerizable materials may be polymerized merely upon exposure to sunlight. Therefore, depending upon how the photoinitiator is designed, the photoinitiator of the present invention can eliminate the cost of purchasing and maintaining light sources in numerous industries wherein such light sources are necessary without the photoinitiators of the present invention.

The effective tuning of the photoinitiators of the present invention for a specific wavelength band permits the photoinitiators of the present invention to more efficiently utilize the target radiation in the emission spectrum of the radiating source corresponding to the "tuned" wavelength band, even though the intensity of such radiation may be much lower than, for example, radiation from a narrow band emitter, such as an excimer lamp. For example, it may be desirable to utilize an excimer lamp, or other radiation emission source, that emits radiation having a wavelength of approximately 360 nm or 420 nm with the photoinitiators of the present invention. However, the effectiveness of the photoinitiators of the present invention is not necessarily dependent upon the availability or use of a narrow wavelength band radiation source.

Use of the Above-Described Photoinitiators in an Ink Composition

The above-described photoinitiators of the present invention may be incorporated into ink compositions. In one embodiment of the present invention, one or more of the photoinitiators are incorporated into an ink jet ink composition for use on ink jet ink printers. The ink

composition may be used on commercially available ink jet printing machines alone or in combination with a radiation source in series with the ink jet printing machine for instantaneous curing of the ink jet ink composition. Any radiation source known to those of ordinary skill in the art may be used to cure the ink jet ink composition. Desirably, one of the above-described radiation sources is used to cure the ink composition.

Use of the Above-Described Photoinitiators in Other Radiation-Drying Printing Process

A further use of the above-described photoinitiators of the present invention involves the incorporation of one or more of the photoinitiators into an ink composition for use on a radiation-drying printing press. As discussed above, "radiation-drying printing" refers to any printing method which utilizes radiation as a drying means. Radiation-drying printing includes, for example, off-set printing operations, such as on a Heidelberg press, flexographic printing, and flat-bed printing.

The photoinitiators of the present invention enable increased press output due to the photoreactivity of the photoinitiators. Further, the increased output may be obtained while using a minimal amount of photoinitiator and a low energy light source. In one embodiment of the present invention, complete curing at an output rate of 10,000 printed sheets per hour may be obtained using a 50 W cold lamp as the light source.

Any of the above-described photoinitiators may be used in the printing processes disclosed herein. Desirably, the amount of photoinitiator added to the ink composition, adhesive composition or resin is less than about 4.0 wt% of the total weight of the composition. More desirably, the amount of photoinitiator added to the composition is from about 0.25 to about 3.0 wt% of the total weight of the

composition. Most desirably, the amount of photoinitiator added to the composition is from about 0.25 to about 2.0 wt% of the total weight of the composition.

5 A major advantage of the photoinitiators of the present invention is that they enable rapid curing times of ink compositions, adhesive compositions and/or resins in comparison to the curing times of prior art photoinitiators. Ink compositions containing the photoinitiators of the present invention possess rapid curing times from 5-10 times faster than the curing times of ink compositions containing the best known photoinitiators. The use of the photoinitiators of the present invention in ink compositions, adhesive compositions or resins for printing presses enables print speeds, which were at one time thought to be unobtainable. For example, in an open air printing process using a Heidelberg print press and a 50 W excimer cold lamp for photocuring, desirably the printed sheet output is greater than 6,000 sheets per hour. More desirably, the printed sheet output is greater than 8,000 sheets per hour. Most desirably, the printed sheet output is greater than 10,000 sheets per hour.

The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or the scope of the present invention. In the examples, all parts are by weight, unless stated otherwise.

COMPARATIVE EXAMPLE 1

Photocuring of CGI 369 in Red Flexo Resin

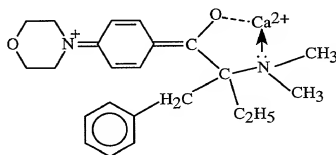
30 A mixture of Ciba Geigy photoinitiator 369 (CGI 369) in the form of a powder was added to a 1 g sample of red flexo ink (Gamma Graphics). The mixture was exposed to UV radiation while positioned within an FTIR machine to

monitor the decrease in carbon-carbon double bonds within the mixture. The curing rate was measured.

EXAMPLE 1

Photocuring of One of KC's New Photoinitiators in Red Flexo Resin

A mixture of Kimberly Clark's photoinitiator, having the following structure, in the form of a powder was added to a 1 g sample of red flexo ink (Gamma Graphics).

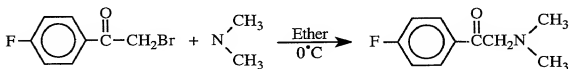


The mixture was exposed to UV radiation while positioned within an FTIR machine to monitor the decrease in carbon-carbon double bonds within the mixture. The curing rate was measured. The photoinitiator had a curing rate relative to the CGI 369 photoinitiator of greater than 220%.

EXAMPLE 2

Method of Forming a 1-(p-fluorophenyl)-2-dimethylamine-ethanone Intermediate to a Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:

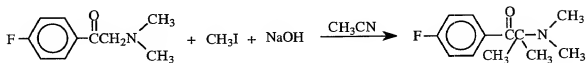


Into a three-necked round-bottom flask was placed 200 ml of anhydrous diethyl ether with stirrer bar and bubbler inlet. The ether was cooled to 0°C. Dimethyl amine was bubbled into the solvent for 1 hour to make a saturated solution. Into the flask was placed 10.0 g (0.046 mole) of 1-p-fluorophenacyl bromide dissolved in 50 ml of ether over a period of about 20 minutes. The temperature of the mixture was kept at 0°C for about 4 hours and then allowed to raise to room temperature overnight. The reaction mixture was then filtered to remove the dimethyl amine hydroxide and the solvent to yield a yellow oil. The oil was pumped in a vacuum oven and used in further examples without further purification. The final product was 1-(p-fluorophenyl)-2-dimethylamine-ethanone and the yield of the reaction was 7.5 g of oil (94%).

EXAMPLE 3

Method of Forming a 1-(p-fluorophenyl)-2-dimethylamine-2-methyl-propanone Intermediate to a Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:



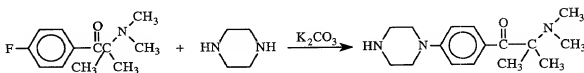
Into a 1-liter, round-bottom flask was placed 5.0 g (0.028 mole) of the 1-(p-fluorophenyl)-2-dimethylamine-ethanone compound of Example 1, 8.6 g (0.062 mole) of methyl iodide, and 330 ml of acetonitrile. The reaction mixture was stirred for about 4 hours. The solvent was then removed and replaced with 300 ml of water and 7.3 g of a 34 wt% solution of sodium hydroxide (0.07 mole). The reaction mixture was then heated at about 55°C to 60°C for about 1 hour. On cooling, the reaction mixture was extracted with

ether, and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield an oil which was pumped in the vacuum oven. The product crystallized in a refrigerator overnight. The final product was measured to be 4.1 g of 1-(p-fluorophenyl)-2-dimethylamine-2-methylpropanone and the yield was found to be about 71%.

EXAMPLE 4

Method of Forming a Piperazine-Containing Intermediate to a Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:

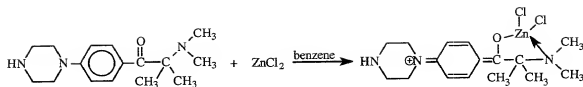


Into a 250 ml, round-bottom flask was placed 1.4 g (0.01 mole) of potassium carbonate, 2.0 g of the product from Example 2, 0.86 g (0.01 mole) of piperazine, and 20 ml of N,N-dimethylformamide (DMF). The mixture was flushed with argon for about 20 minutes prior to heating at reflux. The reaction mixture was heated at reflux for about 16 hours. HPLC indicated a 80% conversion to the desired product shown below (This was the only compound having a 325 nm UV absorption peak.) The crude product was recrystallized from ethanol to yield a pale yellow solid. The yield of the reaction was 1.8 g of 1-piperazine-2-dimethylamine-2-methylpropanone (69%).

EXAMPLE 5

Method of Forming a Zn-Containing Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:



5 In order to form one of the photoinitiators of the present invention, zinc chloride containing water was heated under an argon gas atmosphere to produce zinc chloride free of water. Into a 250 ml, three-necked, round-bottom flask fitted with condenser, argon gas inlet, and bubbler outlet was placed 2.6 g (0.019 mole) of ZnCl_2 . The flask was continuously flushed with argon while the ZnCl_2 was heated with a propane torch. The ZnCl_2 was heated for about 15 minutes until it melted. Heating was continued for about ten minutes and then the ZnCl_2 was allowed to cool under an argon atmosphere. The product was ground to form a powder, still under an argon atmosphere.

10 The resulting ZnCl_2 , 80 ml of benzene, and 8 g of the 1-morpholino-2-dimethylamine-2-methyl-propanone produced in Example 4 were heated at reflux for about 12 hours in an argon atmosphere. The solution was then cooled and filtered. The solvent was removed under reduced pressure to yield a yellow powder. The powder was pumped in a vacuum oven at ambient temperature to yield 6.9 g of photoinitiator (yield 79%) having the structure above.

25 Samples of the yellow solid were mixed into offset black resins (GERBER-SCHMIDT GmbH, Frankfurt, Germany) at 2.0 wt% based on the total weight of the resin. The resins were drawn down into a thin film and exposed to an excimer lamp (308 nm). The resins fully cured after 1-2 flashes (0.05 seconds/flash). The control prepared with

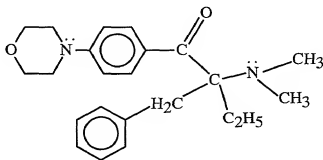
IRGACURE® 369 (available from Ciba Geigy) took 6-8 flashes and was still not fully cured.

EXAMPLE 6

Method of Forming a New Zn-Containing Photoinitiator

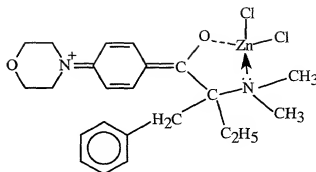
In order to form one of the photoinitiators of the present invention, zinc chloride containing water was heated under an argon gas atmosphere to produce zinc chloride free of water. Into a 1-liter, three-necked flask was placed 7.4 g (0.05 mole) of ZnCl_2 . The flask was continuously flushed with argon while the ZnCl_2 was heated with a propane torch. The ZnCl_2 was heated until it liquified. Heating was continued for about ten minutes and then the ZnCl_2 was allowed to cool. The product was ground to form a powder, still under an argon atmosphere.

The resulting ZnCl_2 , 200 ml of benzene, and 20 g (0.05 mole) of IRGACURE® 369 (available from Ciba Geigy) having the following structure



were heated at reflux for about 12 hours in an argon atmosphere. The solution was then cooled and filtered. The solvent was removed under reduced pressure.

The resulting modified-369 compound had the following structure:



The yellow solid was found to have a similar retention time and UV absorption compared to IRGACURE® 369. However, the cure rate of a resin containing the yellow solid was 3 to 5 times faster than the cure rate of an identical resin containing the IRGACURE® 369 photoinitiator.

Samples of the yellow solid were mixed into offset and flexo resins (GERBER-SCHMIDT GmbH, Frankfurt, Germany) at 2.0 and 3.0 wt% based on the total weight of the resin. The resins were printed onto white plates and exposed to an excimer lamp (308 nm) or a mercury lamp (360 nm). The resins rapidly cured.

EXAMPLE 7

Method of Forming a New BF₃-Containing Photoinitiator

Into a 1-liter, three-necked flask was placed 100 g (0.275 mole) of IRGACURE® 369 and 500 ml of dry benzene. The flask was continuously flushed with argon and cooled in an ice bath. Into the flask was added 38.8 g (0.0275 mole) of boron trifluoride etherate. The reaction was carried out in the dark and stirred at 0°C for about 10 hours.

A yellow precipitate formed and was filtered. The solvent was removed under reduced pressure to yield 82.1 g (69% yield) of a yellow solid.

HPLC indicated a different retention time and a UV absorption at about 415 nm.

Samples of the yellow solid were mixed into offset and flexo resins at 2.0 and 3.0 wt% based on the total weight of the resin. The resins were rapidly cured when printed onto white plates and exposed to a Fusion Systems 'V' Bulb (420 nm).

EXAMPLE 8

Method of Forming a New BCl₃-Containing Photoinitiator

Into a 1-liter, three-necked flask was placed 10 g (0.027 mole) of IRGACURE® 369 and 50 ml of dry benzene. The flask was continuously flushed with argon and cooled in an ice bath. Into the flask was added 3.16 g (0.027 mole) of boron trichloride in xylene. The reaction was stirred overnight at 0°C for about 10 hours.

A yellow precipitate formed and was filtered. The solvent was removed under reduced pressure to yield 11.2 g (86% yield) of a yellow solid.

HPLC indicated a retention time and a UV absorption similar to IRGACURE® 369.

Samples of the yellow solid were mixed into offset resins at 2.0 wt% based on the total weight of the resin. The resins were rapidly cured when drawn down onto white plates and exposed to an excimer lamp (308 nm).

EXAMPLE 9

Offset Printing Using Photoinitiators of the Present Invention

Two lots of Zn-containing photoinitiator were prepared as in Examples 2-5 above. The lots were designated Z1029 and Z106. Offset printing trials were performed at the Institute for Surface Modification (Leipzig, Germany) using Gerber Schmidt highly pigmented black ink compositions.

The photoinitiator was added to the ink composition and mixed using a high speed vortex mixer. After mixing for about 15 minutes, the temperature was measured to be about 60°C. Similar ink compositions were prepared using IRGACURE® 369.

A sheet-fed offset press manufactured by Heidelberg Press, Model No. GT052, was used to print sheets using the above ink compositions. The press ran up to 8,000 sheets per hour. The curing took place in a nitrogen atmosphere or in air. The results of the printing test are given below in Table 1.

Table 1. Cure Results of Offset Printing

Photoinitiator	Observations
4.0 wt% PI 369	Resin was soft. 95% cured.
4.0 wt% PI 369 ***	Resin was soft, poorly cured.
1.0 wt% PI 369	Resin was very poor, even wet.
4.0 wt% Z1029	Resin was poor. 70 to 80% cured.
3.0 wt% Z1029	Resin was better, but still soft. 80% cured.
2.0 wt% Z1029	Resin was even better. 85% cured.
1.0 wt% Z1029	Resin was better than the PI 369. 90% cured.
0.75 wt% Z1029 and 0.25 wt% PI 369	Good surface cure, but soft under the surface.
1.0 wt% Z1029 and 0.25 wt% PI 369	Good surface cure. 95% cured.
1.0 wt% Z1029 and 0.25 wt% PI 369 ***	Good surface cure. 95% cured.
1.0 wt% Z1029 and 0.5 wt% PI 369	Hard surface cure. 100% cured.
1.0 wt% Z1029 and 0.5 wt% PI 369 ***	Good surface cure. 95% cured.
1.0 wt% Z1029 and 0.5 wt% PI 369	Hard solid cure. 100% cured.
1.0 wt% Z1029 and 0.5 wt% PI 369 ***	Good surface cure. Soft under the surface. 90% cured.

1.0 wt% Z1029 and 0.75 wt% PI 369	Hard solid cure. 100% cured.
1.0 wt% Z1029 and 0.75 wt% PI 369 ***	Good surface cure. Good cure under the surface. 98% cured.
1.0 wt% Z1029 and 1.0 wt% PI 369	Hard solid cure. 100% cured.
1.0 wt% Z1029 and 1.0 wt% PI 369 ***	Good surface cure. Good cure under the surface. 96% cured.

*** Test was run in air, as opposed to a nitrogen atmosphere.

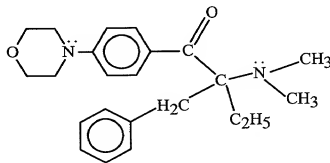
As shown in Table 1, photoinitiator systems of the present invention consistently provided better cure than IRGACURE® 369 alone. The photoinitiators of the present invention provided good cure results in a nitrogen atmosphere, as well as, in air.

EXAMPLE 10

Method of Forming a New Cationic Photoinitiator

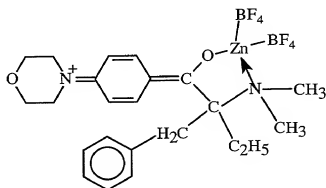
In order to form one of the photoinitiators of the present invention, zinc tetrafluoroborate (available from Aldrich) was heated overnight at 50°C in a vacuum oven (0.01 mm Hg) to produce zinc tetrafluoroborate free of water. The dried solid and ether were mixed to form a 0.5M solution of zinc tetrafluoroborate in ether.

Four grams (0.01 mole) of IRGACURE® 369 (available from Ciba Geigy) having the following structure



was dissolved in 100 ml of ether (anhydrous) in a three-necked round bottom flask fitted with stirrer bar, argon gas bubbler, and condenser. To this solution was added, via a syringe, 21.5 ml of the 0.5M $\text{Zn}(\text{BF}_4)_2$ ether solution over 10 minutes. The clear solution turned cloudy. A white precipitate formed over a period of an hour. The white precipitate was filtered on a Buckner funnel and washed with 100 ml of anhydrous ether. The powder was then pumped in a vacuum for over an hour at room temperature.

The resulting compound had the following structure:



EXAMPLE 11

Curing Process Using a Cationic Photoinitiator

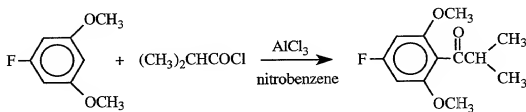
In a beaker 8.5 g of CYRACURE® UVR-6110 (cycloaliphatic diepoxide, available from Union Carbide) was heated to 50°C while stirring with a magnetic stirrer. Into the beaker was added 0.1 g of the photoinitiator produced from Example 1, which was allowed to dissolve over a period of 2 minutes. Into the beaker, 2.5 g of UCAR-VAGH (vinyl chloride-vinyl acetate-vinyl alcohol terpolymer, available from Union Carbide) was slowly added while stirring resulting in a clear solution after about 3 minutes.

A drop of the mixture was drawn down onto a metal plate. The film was exposed to a medium pressure mercury arc lamp. The film immediately went from being tacky to fully cured.

EXAMPLE 12

Method of Forming a 1-(2,6-dimethoxy-4-fluorophenyl)-2-methylpropan-1-one Intermediate to a Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:

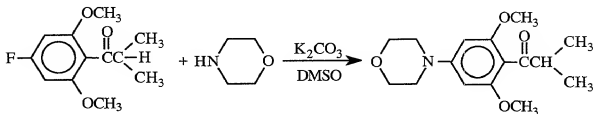


Into a 1-liter, three-necked round-bottom flask was placed 20.0 g (0.13 mole) of 1,3-dimethoxy-5-fluorobenzene, 13.6 g (0.013 mole) of 2-methylpropanoyl chloride, and 100 ml of nitrobenzene. The mixture was flushed with argon and an equal molar amount of AlCl_3 (17.2 g) was added to the reaction mixture while stirring at 5°C . The mixture was stirred at a temperature of 5°C for about 1 hour after the addition of the AlCl_3 . The reaction mixture was then mixed with about 100 ml of distilled water and extracted with dichloromethane. The organic layer was washed with NaHCO_3 solution, salt water, and then dried. The solvent was removed by vacuum to yield the final product, 1-(2,6-dimethoxy-4-fluorophenyl)-2-methylpropan-1-one. The yield of the reaction was 22.8 g of product (77%).

EXAMPLE 13

*Method of Forming a Morpholino-Containing
Intermediate to a Photoinitiator of the Present Invention*

The following reaction was carried out as detailed below:

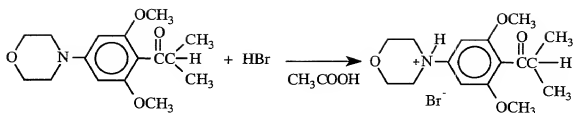


Into a 1-liter, three-necked round-bottom flask was placed 15.0 g (0.07 mole) of 1-(2,6-dimethoxy-4-fluorophenyl)-2-methylpropan-1-one produced in Example 12, 5.8 g (0.07 mole) of morpholine, and 19.0 g (0.14 mole) of K_2CO_3 in 100 ml. of dimethylsulfoxide (DMSO). The mixture was flushed with argon and heated to reflux overnight. The reaction mixture was cooled and then mixed with about 100 ml of distilled water and extracted with dichloromethane. The organic layer was washed with $NaHCO_3$ solution, salt water, and then dried. The solvent was removed by vacuum to yield the final product, 1-(2,6-dimethoxy-4-morpholinophenyl)-2-methylpropan-1-one. The yield of the reaction was 18.1 g of product (88%).

EXAMPLE 14

*Method of Forming a Morpholino-Containing Bromide
Salt Intermediate to a Photoinitiator of the Present
Invention*

The following reaction was carried out as detailed below:

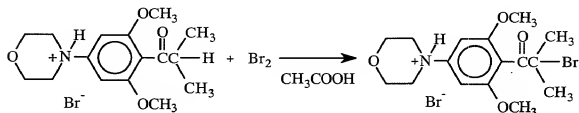


Into a 1-liter, three-necked round-bottom flask was placed 15.0 g (0.05 mole) of 1-(2,6-dimethoxy-4-morpholinophenyl)-2-methylpropan-1-one produced in Example 13 and 150 ml. of glacial acetic acid. Hydrogen bromide gas was bubbled through the mixture for about 40 minutes. The product was then used in the next step, disclosed in Example 15.

EXAMPLE 15

Method of Forming a Morpholino-Containing Bromide-Containing Salt Intermediate to a Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:



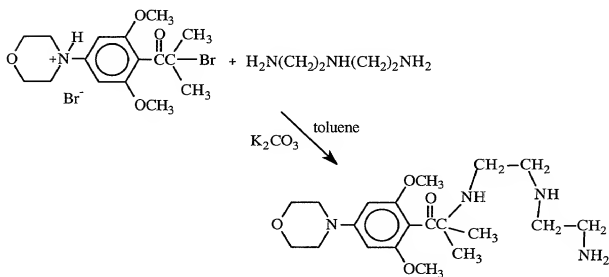
Into a 1-liter, three-necked round-bottom flask was placed 19.1 g (0.05 mole) of the product produced in Example 14. The mixture was chilled to 5°C. To the chilled mixture was added dropwise 8.0 g of Br₂ over a period of about one hour. The mixture was then stirred for about one hour. The solvent was removed under vacuum to yield a pale

yellow/orange solid. The yield of the final product was 20.9 g of product (92%).

EXAMPLE 16

Method of Forming a Morpholino-Containing Bromide-Containing Salt Intermediate to a Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:

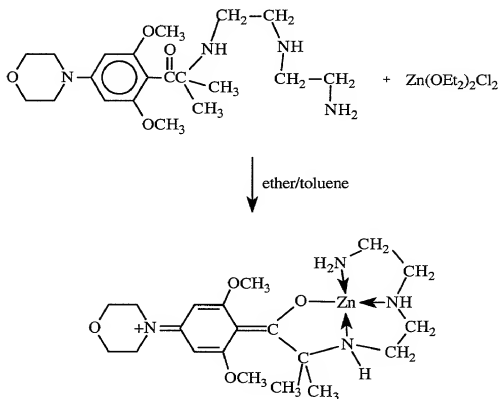


Into a 1-liter, three-necked round-bottom flask was placed 15.0 g (0.03 mole) of the product produced in Example 17, 3.1 g (0.03 mole) of diethylenetriamine, 8.2 g (0.06 mole) of K_2CO_3 , and 100 ml. of toluene. The mixture was heated at reflux overnight. The solvent was removed under vacuum to yield a yellow solid. The yield of the final product was 8.7 g of product (74%).

EXAMPLE 17

Method of Forming a Zn-complex Photoinitiator of the Present Invention

The following reaction was carried out as detailed below:



Into a 1-liter, three-necked round-bottom flask was placed 5.0 g (0.013 mole) of the product produced in Example 18 and 50 ml. of toluene. To the mixture was slowly added 1.72 g (0.013 mole) of $\text{Zn}(\text{OEt}_2)_2\text{Cl}_2$ in ether (i.e., 21 ml. of a 0.6M solution of $\text{Zn}(\text{OEt}_2)_2\text{Cl}_2$ in ether). The reaction materials were stored for about one hour at room temperature. The solvent was removed under vacuum to yield a yellow solid. The yield of the final product was 5.4 g of product (96%).

EXAMPLE 18

*Testing of Zn-Containing Photoinitiator of the Present
Invention in a Red Flexographic Resin*

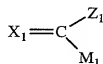
5 A sample containing 0.1 g of the photoinitiator
produced in Example 19 and 1.0 g of a red flexographic
resin was prepared. A drop of the resin sample was drawn
down on a white panel. The thin film was exposed to a 50W
excimer lamp (308 nm). The resin fully cured after 4 flashes
10 (0.01 seconds/flash).

While the specification has been described in detail
with respect to specific embodiments thereof, it will be
appreciated that those skilled in the art, upon attaining an
15 understanding of the foregoing, may readily conceive of
alterations to, variations of, and equivalents to these
embodiments. Accordingly, the scope of the present
invention should be assessed as that of the appended claims
and any equivalents thereto.
20

Claims

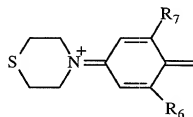
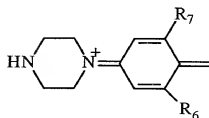
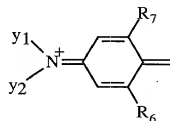
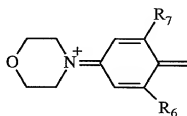
What is claimed is:

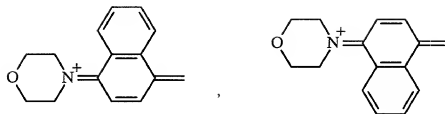
- 5 1. A photoinitiator having the following formula:



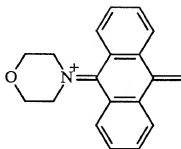
10 wherein X_1 comprises a conjugated system of one or more aryl groups or substituted aryl groups; Z_1 comprises -O, -S, an alkyl group having from one to six carbon atoms, an ester moiety, a ketone moiety, an amine moiety, an imine moiety, an ether moiety, an aryl or substituted aryl group, a metal or non-metal, or a metal or non-metal containing group; and M_1 comprises an alkyl group, a substituted alkyl group, or forms a five-member ring with Z_1 .

- 15 2. The photoinitiator of Claim 1, wherein X_1 comprises





or



wherein R_6 and R_7 , each independently represent hydrogen, an alkyl group having from one to six carbon atoms, an alkoxy group having from one to six carbon atoms, or a halogen-substituted alkyl group; and wherein y_1 and y_2 each independently represent a hydrogen, an alkyl group having from one to six carbon atoms, an aryl group,



or



wherein X_3 represents a hydrogen, an alkyl or substituted alkyl group, or an aryl or substituted aryl group.

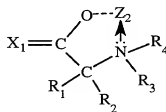
4. The photoinitiator of Claim 1, wherein M_1 comprises a tertiary alkyl group having the following formula:



wherein y_3 , y_4 and y_5 each independently represent a hydrogen, an alkyl group having from one to six carbon atoms, a tertiary amine group, an aryl group, or a substituted aryl group.

5. The photoinitiator of Claim 1, wherein M_1 and Z_1 form a five-member ring.

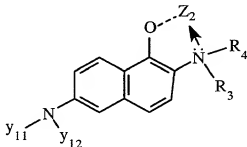
6. The photoinitiator of Claim 5, wherein the photoinitiator has the following structure:



wherein Z_2 is a metal or non-metal atom, a metal or non-metal containing salt, or $-C(O)R$, which forms a covalent bond with the oxygen atom; R , R_3 and R_4 are each independently a hydrogen atom, an alkyl or substituted alkyl group, or an aryl or substituted aryl group; and R_1 and R_2 are each independently a hydrogen atom, an alkyl or

substituted alkyl group, or an aryl or substituted aryl group, or form one or more aromatic rings with X_1 .

- 5 7. The photoinitiator of Claim 6, wherein R_1 , R_2 , and X_1 form a photoinitiator having the structure below:



wherein y_{11} and y_{12} are each independently represent a hydrogen, an alkyl group having from one to six carbon atoms, an aryl group,

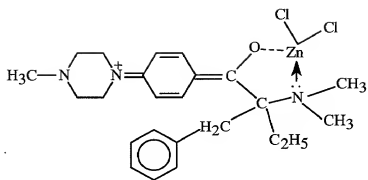


or

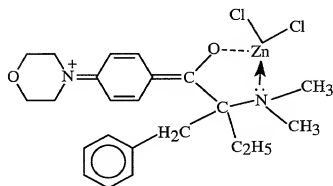


wherein X_3 represents a hydrogen, an alkyl or substituted alkyl group, or an aryl or substituted aryl group.

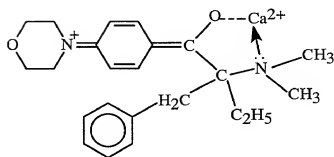
8. The photoinitiator of Claim 6, wherein the photoinitiator comprises



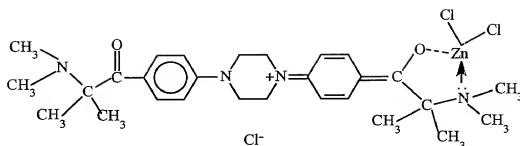
or



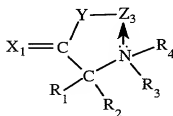
or



or

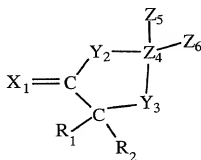


9. The photoinitiator of Claim 5, wherein the photoinitiator has the following structure:



wherein Y is $-O-$ or $-N(R_5)-$; Z_3 is a metal or nonmetal cation or a salt containing the cation; R_3 and R_4 are each independently a hydrogen atom, an alkyl or substituted alkyl group, or an aryl or substituted aryl group; and R_1 and R_2 are each independently a hydrogen atom, an alkyl or substituted alkyl group, or an aryl or substituted aryl group, or form one or more aromatic rings with X_1 .

10. The photoinitiator of Claim 5, wherein the photoinitiator has the following structure:

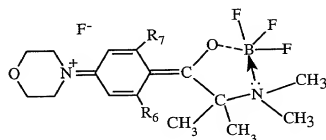


wherein Y_2 and Y_3 each independently represent $-O-$ or $-N(R_3)(R_4)-$; R_3 and R_4 are each independently a hydrogen atom, an alkyl or substituted alkyl group, or an aryl or substituted aryl group; R_1 and R_2 are each independently a hydrogen atom, an alkyl or substituted alkyl group, or an aryl or substituted aryl group or form one or more aromatic rings with X_1 ; Z_4 is a metal or nonmetal atom; and Z_5 and Z_6 are halogen-containing anions or form one or more rings with or without R_3 or R_4 .

11. The photoinitiator of Claim 10, wherein Z_4 comprises Cd, Hg, Zn, Mg, Al, Ga, In, Tl, Sc, Ge, Pb, Si, Ti, Sn, Zr, boron or phosphorus.

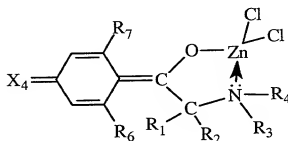
12. The photoinitiator of Claim 10, wherein Z_5 and Z_6 each independently comprise fluorine, chlorine or bromine-containing anions.

13. The photoinitiator of Claim 10, wherein the photoinitiator comprises



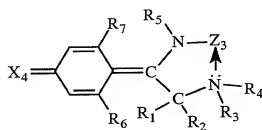
wherein R_6 and R_7 each independently represent hydrogen, an alkyl group having from one to six carbon atoms, an alkoxy group having from one to six carbon atoms, or a halogen-substituted alkyl group.

14. The photoinitiator of Claim 10, wherein the photoinitiator has the following structure:



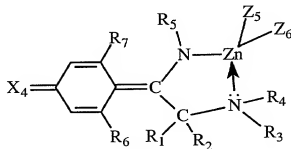
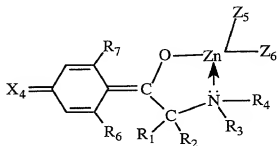
wherein X_4 comprises any nitrogen-containing group, which donates a pair of electrons to the nitrogen-carbon double bond; and R_6 and R_7 each independently represent hydrogen, an alkyl group having from one to six carbon atoms, an alkoxy group having from one to six carbon atoms, or a halogen-substituted alkyl group.

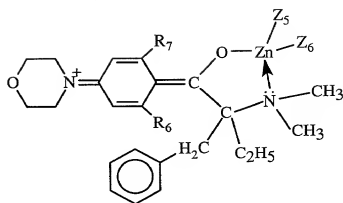
15. The photoinitiator of Claim 9, wherein the photoinitiator has the following structure:



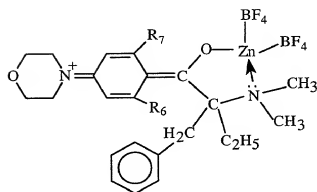
wherein X_4 comprises any nitrogen-containing group, which donates a pair of electrons to the nitrogen-carbon double bond; and R_6 and R_7 each independently represent hydrogen, an alkyl group having from one to six carbon atoms, an alkoxy group having from one to six carbon atoms, or a halogen-substituted alkyl group.

16. The photoinitiator of Claim 10, wherein the photoinitiator has the following structure:





or



17. A method of generating a reactive species,
comprising:

irradiating the cationic photoinitiator of Claim 1
with radiation.

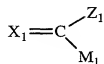
18. A method of polymerizing a polymerizable
material, comprising:

irradiating an admixture of a polymerizable
material and the photoinitiator of Claim 1.

NOVEL PHOTOINITIATORS AND APPLICATIONS THEREFOR

Abstract of the Disclosure

5 The present invention is directed to new, energy-efficient, photoinitiators having the following general formula:



10 wherein of X_1 is a conjugated system such as one or more aryl groups or substituted aryl groups; Z_1 is $-\text{O}$, $-\text{S}$, an alkyl group having from one to six carbon atoms, an ester moiety, a ketone moiety, an amine moiety, an imine moiety, an ether moiety, an aryl or substituted aryl group, a metal or non-metal, or a metal or non-metal containing group, such as a
15 zinc-containing group or a boron-containing group, respectively; and M_1 is an alkyl group, a substituted alkyl group, or forms a five-member ring with Z_1 . The present invention is also directed to a method of generating a reactive species, which includes exposing one or more
20 photoinitiators to radiation to form one or more reactive species. Also described are methods of polymerizing polymerizable materials, methods of curing an unsaturated oligomer/monomer mixture, and methods of laminating using the photoinitiators of the present invention. In
25 addition, the present invention is directed to ink compositions, adhesive compositions and resins, and methods of printing using the above-described photoinitiators.